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AIR POLLUTION ASPECTS OF HYDROCHLORIC ACID

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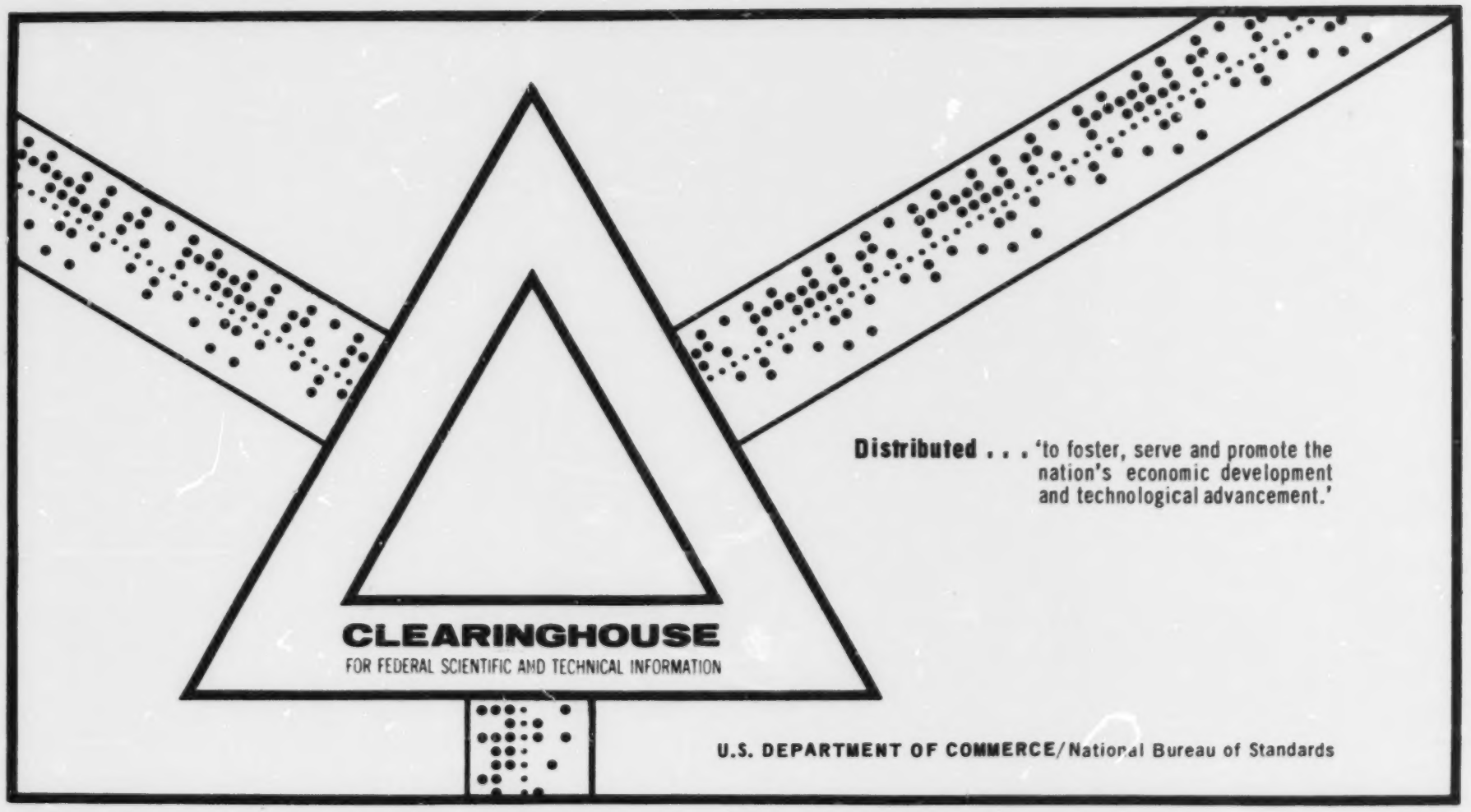
Bethesda, Maryland

September 1969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AIR POLLUTION ASPECTS
OF
HYDROCHLORIC ACID

Prepared for the
National Air Pollution Control Administration
Consumer Protection & Environmental Health Service
Department of Health, Education, and Welfare
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FOREWORD

As the concern for air quality grows, so does the concern over the less ubiquitous but potentially harmful contaminants that are in our atmosphere. Thirty such pollutants have been identified, and available information has been summarized in a series of reports describing their sources, distribution, effects, and control technology for their abatement.

A total of 27 reports have been prepared covering the 30 pollutants. These reports were developed under contract for the National Air Pollution Control Administration (NAPCA) by Litton Systems, Inc. The complete listing is as follows:

Aeroallergens (pollens)
Aldehydes (includes acrolein and formaldehyde)
Ammonia
Arsenic and Its Compounds
Asbestos
Barium and Its Compounds
Beryllium and Its Compounds
Biological Aerosols (microorganisms)
Boron and Its Compounds
Cadmium and Its Compounds
Chlorine Gas
Chromium and Its Compounds (includes chromic acid)
Ethylene
Hydrochloric Acid
Hydrogen Sulfide
Iron and Its Compounds
Manganese and Its Compounds
Mercury and Its Compounds
Nickel and Its Compounds
Odorous Compounds
Organic Carcinogens
Pesticides
Phosphorus and Its Compounds
Radioactive Substances
Selenium and Its Compounds
Vanadium and Its Compounds
Zinc and Its Compounds

These reports represent current state-of-the-art literature reviews supplemented by discussions with selected knowledgeable individuals both within and outside the Federal Government. They do not however presume to be a synthesis of available information but rather a summary without an attempt to interpret or reconcile conflicting data. The reports are

necessarily limited in their discussion of health effects for some pollutants to descriptions of occupational health exposures and animal laboratory studies since only a few epidemiologic studies were available.

Initially these reports were generally intended as internal documents within NAPCA to provide a basis for sound decision-making on program guidance for future research activities and to allow ranking of future activities relating to the development of criteria and control technology documents. However, it is apparent that these reports may also be of significant value to many others in air pollution control, such as State or local air pollution control officials, as a library of information on which to base informed decisions on pollutants to be controlled in their geographic areas. Additionally, these reports may stimulate scientific investigators to pursue research in needed areas. They also provide for the interested citizen readily available information about a given pollutant. Therefore, they are being given wide distribution with the assumption that they will be used with full knowledge of their value and limitations.

This series of reports was compiled and prepared by the Litton personnel listed below:

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Appreciation is expressed to the many individuals both outside and within NAPCA who provided information and reviewed draft copies of these reports. Appreciation is also expressed to the NAPCA Office of Technical Information and Publications for their support in providing a significant portion of the technical literature.

ABSTRACT

Hydrochloric acid irritates the membranes of the eye and upper respiratory tract, and prolonged exposure to low concentrations can cause erosion of the teeth. Severe exposures can result in pulmonary edema and laryngeal spasm, both of which can be fatal. There are no known chronic or acute systemic effects of hydrochloric acid. Hydrochloric acid is also a phytotoxicant, and its emissions have been responsible for plant damage in several instances. Recent data indicate that it is a stronger phytotoxicant than reported in the earlier literature.

The acid is strongly corrosive to most metals. Hydrogen chloride gas emissions are readily converted to hydrochloric acid by the moisture in the air. Hydrogen chloride is a by-product of many organic chlorinating reactions; in some instances the hydrogen chloride is collected for use, but in small operations it may not be economically feasible to recover the gas. Hydrogen chloride emissions result from the burning of coal, chlorinated plastics, and paper. No information has been found on the concentration of hydrochloric acid in the atmosphere. The major uses of hydrogen chloride or hydrochloric acid are in manufacturing chemicals, producing metals, and acidizing oil wells. Effective control of emissions can be

accomplished by the use of water scrubbing equipment.

No information has been found on costs for obtaining and maintaining the control equipment and economic losses due to hydrochloric acid emissions. Methods of analysis for hydrochloric acid are based on determining the acidity or the chloride content of samples, and therefore, other strong acids or chloride salts may cause interference.

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1. INTRODUCTION

Hydrogen chloride (HCl) is a hygroscopic, colorless gas with a strong, pungent, and irritating odor. Because of its high solubility in water, the gas fumes in moist air. An aqueous solution of hydrogen chloride is called hydrochloric acid. Emissions of hydrogen chloride are readily converted to hydrochloric acid fumes and droplets in air or when inhaled into the lungs. The strong dehydrating properties of hydrogen chloride can result in serious burns of the skin or mucous membranes. Hydrochloric acid is extremely corrosive to most materials. (See Table 2 in the Appendix for the properties of hydrogen chloride and hydrochloric acid.)

Inhalation of hydrochloric acid causes coughing and choking, as well as inflammation and ulceration of the upper respiratory tract. Irritation of the eye membranes is another effect, and exposure to high concentrations can cause clouding of the cornea. The teeth can also be affected, and erosion may result. Hydrogen chloride and hydrochloric acid are also phytotoxicants that damage the leaves of a great variety of plants. Several episodes of plant damage from hydrochloric acid emissions have been reported.

The possible sources of emissions of hydrogen chloride or hydrochloric acid are not only their commercial production

and use, but also the burning of paper products and fossil fuels. Many industries also produce hydrochloric acid as an unwanted by-product in the manufacture of chemicals. The emissions can be effectively controlled with the available methods, which usually involve the use of water scrubbing equipment.

2. EFFECTS

2.1 Effects on Humans

Little information is available on the toxicity of hydrogen chloride or hydrochloric acid when inhaled by humans. Most of the information cited in the literature was obtained from studies conducted 30 to 80 years ago pertaining to occupational exposure.

2.1.1 Toxicity

Hydrochloric acid primarily irritates and attacks the membranes of the eyes and upper respiratory tract.[34,73] The effects increase in severity from irritation to pulmonary edema, and even to death in extreme cases, depending upon the concentration and duration of exposure. No organic damage results from exposure to 7,000 $\mu g/m^3$ (5 ppm*).[113] Irritation of mucous membranes occurs at 15,000 $\mu g/m^3$ (10 ppm),[113] although workers accustomed to hydrochloric acid exposure can work undisturbed at this concentration.[45,72] Work becomes difficult, but not impossible, in the concentration range of 15,000 to 75,000 $\mu g/m^3$ (10 to 50 ppm),[45,72] and irritation of the throat membranes has been reported at exposures of 50,000 $\mu g/m^3$ (35 ppm).[87] Work becomes impossible at levels above 75,000 $\mu g/m^3$,[72] and exposure to levels of 75,000 to 150,000 $\mu g/m^3$ (50 to 100 ppm) cannot be tolerated by humans for longer than 60 minutes.[44,45,52,87]

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*Conversion factor used in this report: 1 ppm is approximately equal to 1,470 $\mu g/m^3$.

Exposure for only a few minutes at 1,300 to 2,000 ppm may be lethal;[52,87] the acid neutralizes the alkali of the tissues and causes inflammation of the upper respiratory tract, pulmonary edema, or laryngeal spasm, with death possibly resulting.

Mists of hydrochloric acid are not as dangerous to humans as hydrogen chloride gas because the acid has no strong dehydrating effect on the tissues.[87] However, acid mists from heated metal-pickling solutions may cause bleeding of the nose and gums, ulceration of the nasal and oral mucosae, and tenderness of the facial skin so that shaving becomes painful.[45] A study conducted by Toyama et al.[112] of an electrical appliance factory indicated that people not accustomed to hydrochloric acid mists showed a 9 percent decrease in the pulmonary ventilatory peak flow rate when exposed for 1 hour to hydrochloric acid mists (6 μ in diameter), whereas the workers exhibited no change.

Prolonged exposure to low concentrations of hydrochloric acid causes erosion of the teeth.[45] However, there are no known systemic effects, either acute or chronic, from inhalation of hydrochloric acid or hydrogen chloride.[49,87]

The effects of hydrogen chloride on humans are summarized in Table 3 in the Appendix.

2.1.2 Sensory Thresholds

The odor perception threshold values for hydrochloric acid given in the literature include 100 to 200 $\mu g/m^3$ (0.067 to 0.134 ppm), [28,29] 1,500 to 7,500 $\mu g/m^3$ (1 to 5 ppm),[45] and 14,700 $\mu g/m^3$ (10 ppm).[105]

Elfimova[28,29] has studied the threshold reflex of the eyes, respiratory action, and vascular reaction upon exposure to hydrochloric acid aerosols. The results are summarized in Table 3 in the Appendix.

2.1.3 Synergistic Effects

Stayzhkin[85,102] investigated the effect of chlorine and hydrogen chloride gas mixtures on man. In his study of the odor threshold, the effect on reflex reactions of eye sensitivity to light and of optical chronaxy were examined. His results indicated that the two gases acted in combination in an additive manner to produce a perceivable odor when neither gas could be detected alone. The effect is expressed by the following relationship where X must equal one or greater to have a perceivable odor:

$$X = \frac{\text{Concentration } Cl_2}{\text{Odor threshold } Cl_2} + \frac{\text{Concentration HCl}}{\text{Odor threshold HCl}}$$

Furthermore, the physiological and neurological effects of the mixtures were also in the nature of arithmetical summation.

2.2 Effects on Animals

2.2.1 Commercial and Domestic Animals

No reports were found in the literature describing injury to domestic, commercial, or wild animals from exposures to hydrogen chloride or hydrochloric acid in rural or urban environments or near factories that produce or use the acid.

2.2.2 Animal Experiments

Mackle et al.[69] exposed one monkey, three rabbits, and three guinea pigs to 50,000 $\mu g/m^3$ (33 ppm) of hydrogen chloride for a period of 4 weeks (6 hours per day, 5 days per week). None of these animals exhibited immediate toxic effects or pathological changes. However, the authors commented that inhalation of hydrogen chloride daily for one month at 50,000 $\mu g/m^3$ (33 ppm) may be dangerous. Rabbits and guinea pigs were not killed at a concentration of 100,000 $\mu g/m^3$ (67 ppm) for 5 days (6 hours per day). However, it was noted that the guinea pigs were more sensitive to irritant properties of hydrogen chloride than the rabbits, but the rabbits exhibited more pulmonary and nasal damage than the guinea pigs. At higher concentrations, repeated exposures resulted in a weight loss that was proportional to the degree of exposure. A concentration of 1,000,000 $\mu g/m^3$ (670 ppm) of hydrogen chloride for 2 to 6 hours was lethal to rabbits and guinea pigs. Furthermore, 30 minutes' exposure at approximately 6,400,000 $\mu g/m^3$ (4,300 ppm) was lethal to all the animals. At these concentrations, hydrogen chloride causes necrosis of the tracheal and bronchial epithelia and also pulmonary edema, atelectasis, emphysema, and pulmonary blood

vessel damage.[45,69] Production of lesions in the liver and other organs by hydrogen chloride is also described.[69]

After Lehmann[64] exposed cats, rabbits, and guinea pigs to 150,000 to 210,000 $\mu g/m^3$ (100 to 140 ppm) of hydrogen chloride for 6 hours, he found slight corrosion of the cornea and upper respiratory irritation in the animals. Clouding of the cornea occurred after exposure to a concentration of 2,000,000 $\mu g/m^3$ (1,350 ppm) for approximately 90 minutes. After approximately the same exposure time to a concentration of 5,000,000 $\mu g/m^3$ (3,400 ppm), death occurred in 2 to 6 days.

Leitz[65] found that when the respiratory rate is increased by an elevation in environmental temperature, the amount of hydrogen chloride absorption is also increased, thereby heightening the danger of exposure to low concentrations.

Table 4 in the Appendix summarizes the reported effects of hydrogen chloride inhalation by animals.

2.3 Effects on Plants

2.3.1 Phytotoxicity

Haselhoff and Lindau[42] studied the effects of hydrogen chloride and hydrochloric acid on plants after an incident in which plant life was damaged near a factory manufacturing alkali (see Section 2.3.2). Their studies demonstrated that damage to plants from hydrogen chloride resulted from the direct action of the gas itself on the above-ground parts of the plants and not from the conversion products produced in the soil. Fumigation experiments with viburnum and larch seedlings indicated

that approximately 7,500 to 30,000 μg/m^3 (5 to 20 ppm) of hydrogen chloride could kill the plants within 2 days. Moreover, after 1 day at this concentration, the viburnum leaves remained rolled up at the edges, withered, shrunk, faded, and necrotic, even after they were placed in fresh air. Similar injuries resulted from chlorine gas, but a higher concentration of 750,000 μg/m^3 (500 ppm) was necessary to produce damage. Hydrochloric acid fumes (approximately 6 percent acid) required only a few hours to damage the plants, primarily producing bleached spots on the tips or margins of the leaves. At low concentrations of hydrochloric acid (approximately 1 to 10 percent acid), the plants remained healthy for several days.

Further experiments showed that a 1-hour exposure to 1,500,000 μg/m^3 (1,000 ppm) hydrogen chloride produced local lesions in fir, beech, and oak leaves. Marginal leaf scorch was found on the leaves of maple, birch, and pear trees exposed to hydrogen chloride. Tipburn of the fir needles resulting from two exposures to 1,500,000 μg/m^3 (1,000 ppm) was still visible 3 weeks later. The experiments also indicated that spruce was not visibly affected at daily 1-hour exposures to 3,000,000 μg/m^3 (2,000 ppm) hydrogen chloride for 80 days. However, recent studies by Lacasse[61] showed that spruce seedlings died from exposure to less than 50 ppm of hydrogen chloride for only 20 minutes.

Hydrogen chloride injury in broad-leaf plants is indicated by a marginal leaf burn that progresses basipetally with

prolonged exposure.[42] In grasses, the tips become brown-colored after exposure to low concentrations. The threshold concentration for plant marking was suggested to be generally 75,000 to 1,500,000 $\mu g/m^3$ (50 to 100 ppm) hydrogen chloride, but these values were obtained with no air circulation over the plants. Thomas[107] found that the marking threshold for sugar beets was a few hours' exposure at 15,000 $\mu g/m^3$ (10 ppm).

Lacasse et al.[62,74,93] have recently studied the effects of low concentrations of hydrogen chloride on plants. Tomato plants were exposed to 7,500 $\mu g/m^3$ (5 ppm) hydrogen chloride for 2 hours at 31°C, with a relative humidity between 65 and 75 percent, and a light intensity of 3.9×10^4 ergs/cm^2-sec. The leaves developed interveinal bronzing and bleaching, followed by necrosis, within 72 hours after exposure. The middle-aged leaves were affected more severely than the younger leaves. Furthermore, the hydrogen chloride-exposed plants contained 300 percent more chloride than the unexposed control plants. The immature leaves showed the greatest increase in chloride, while the roots and stems showed little or no significant increase. The increase in chloride was not found beyond 24 hours. In fact, there was a slight decrease in chloride content after the first 24 to 72 hours.

Experiments were also conducted to determine the threshold for visible damage of 12 species of coniferous and broadleaf seedlings.[74] The experimental conditions were as follows: exposure to 4,500 to 64,500 $\mu g/m^3$ (3 to 43 ppm) hydrogen chloride

for 4 hours at 27°C, relative humidity between 78 to 85 percent, and light intensity of 1.4 X 10^4 ergs/cm^2-sec. A summary of the threshold values determined by these experiments is given in Table 5 in the Appendix. The results indicate that the coniferous plants were more resistant to incipient injury than the broadleaf plants. Symptoms found in the broadleaf plants included marginal and interveinal necrosis and necrotic flecking. The only symptom observed for the coniferous species was tip necrosis. The period of time for the first appearance of injury varied between 8 and 24 hours.

Lacasse[62] found that the relative humidity of the surrounding area is a very important factor in the damage to plants exposed to hydrogen chloride. Thus, when the relative humidity was increased from 40 to 65 percent, the rate and severity of damage was observed to suddenly increase.

Thomas[107] reported in 1951 that hydrogen chloride is less toxic to plants than sulfur dioxide. Plant responses at high concentrations of hydrogen chloride may resemble acute sulfur dioxide injury.[104]

A summary of the reported effects of hydrogen chloride on plants is given in Table 5 in the Appendix.

2.3.2 Incidents of Plant Damage

Hindawi[46] reported recently that emissions from a glass manufacturing factory injured shrubs, trees, and plants in the surrounding area. Specimens severely injured included maple and cherry trees, rose bushes together with the buds, and begonias.

Factory stack emissions analyzed after the incident contained 178,500 to 709,500 $\mu g/m^3$ (119 to 473 ppm) hydrochloric acid and 1,560 to 2,760 $\mu g/m^3$ (0.52 to 0.92 ppm) chlorine. Analysis of injured silver maples showed a chloride content of 4,700 ppm, compared to 3,800 ppm for uninjured silver maple trees.

Although no other incidents in the United States have been reported, several other countries have reported damage to plants from exposures to hydrochloric acid. The best-known case happened in England.[107] Extensive damage to plants occurred near a factory that used the Leblanc soda process to make alkali and emitted hydrogen chloride as an unwanted by-product. Between 1836 and 1863, scrubbers were installed at various alkali factories which removed 95 percent of the hydrogen chloride in the emissions so that less than 450 $\mu g/m^3$ (30 ppm) of hydrogen chloride remained in the stack effluent. This control eliminated the plant damage.

Bohne[13] reported two examples of damage to plants by emissions of hydrogen chloride from incinerators of nearby hospitals. These incinerators were burning 80 to 90 percent paper and cardboard packing material. In one case, incineration for only 2 to 3 hours per day, 5 days a week, completely ruined the plants in a nursery located 450 meters from the incinerator.

2.4 Effects on Materials

In the literature reviewed, no information was found describing corrosion or damage to materials from exposure to

environmental concentrations of hydrochloric acid. However, it is well-known that hydrochloric acid mists and solutions are extremely corrosive to most metals and alloys.[49,75] Mellor[75] has summarized 24 studies on corrosion of various forms of hard and mild steel and cast iron by hydrochloric acid. He noted that corrosion of cast iron and steel increases regularly as the concentration of the acid increases.

2.5 Environmental Air Standards

The American Conference of Governmental Industrial Hygienists (ACGIH) has adopted 7,000 $\mu g/m^3$ (5 ppm) as the threshold concentration for hydrogen chloride for an 8-hour day, 5-day week.[111]

West Germany has also established 5 ppm as the permissible work-station concentration.[55] West Germany has also established an ambient air quality standard of 0.5 ppm (approximately 700 $\mu g/m^3$) of hydrogen chloride for a 30-minute mean average, with a maximum of 1.0 ppm (1,400 $\mu g/m^3$) of hydrogen chloride for a 30-minute mean average.[55]

Russia has established 15 $\mu g/m^3$ (0.009 ppm) as a 24-hour maximum average for ambient air concentration of hydrogen chloride and a maximum of 50 $\mu g/m^3$ of hydrogen chloride (0.03 ppm) for a single exposure.[55,73] The standard for a 24-hour average is below the concentrations which might cause reflexive reaction of the sensory organs.[86]

Czechoslovakia has established a maximum ambient air concentration which is different from that of Russia. The 24-hour

mean was set at 0.02 ppm, with a one-time exposure maximum of 0.07 ppm.[84]

3. SOURCES

Hydrochloric acid may be emitted from a wide variety of sources. Emissions from some sources may go unnoticed because the hydrochloric acid is generated as an unpredicted product. The sources may be classified as follows:

(1) Direct manufacturing of hydrochloric acid (e.g., acid-salt and synthesis processes),

(2) A predicted by-product of a chlorination process in indirect manufacturing (e.g., by-product process),

(3) Unpredicted or undesired product of a manufacturing process (e.g., thermal decomposition of chloride-containing reactants or products),

(4) Use of hydrochloric acid in the production or manufacturing of other products (e.g., pickling of metals),

(5) Burning or combustion of chloride-containing materials (e.g., fossil fuels, plastics, paper),

(6) Heating of chloride-containing materials (e.g., heating of organic matter).

The first two are described in Section 3.2 as production sources. The fourth source is discussed in Section 3.3 as a product source. Those remaining are discussed in Section 3.4 as other sources.

In a study[3] of air contaminant emissions in Niagara County, N.Y., it was found that 4,083 tons of hydrogen chloride were emitted into the atmosphere per year. Of this total, 2,911 tons originated from processing plants and 1,172 tons from the

consumption of coal and oil for heating purposes. Table 6 in the Appendix lists the total emissions by urban areas within the county.

3.1 Natural Occurrence

Natural occurrences of hydrochloric acid are rare. Almost all of this acid, particularly as an atmospheric pollutant, is produced by man, either from manufacturing processes or burning or heating of chloride-containing substances. Minute quantities of hydrochloric acid are present in nature in volcanic fumes and in some rivers.[58] Of course, it is also present in the gastric juices of the body.

3.2 Production Sources

In the United States, hydrochloric acid is produced by three processes:[7,50,106] (1) the by-product process from chlorination of organic compounds, (2) reaction of chloride salt with sulfuric acid, and (3) synthesis via reaction between chlorine and hydrogen gas. In 1934, 86 percent of the production of hydrochloric acid was by the salt-acid process, 14 percent by the synthesis process, and none from the by-product process.[91] However, in recent years, the by-product process has become the major production source, accounting for over 84 percent of the hydrochloric acid production in 1967.[23] This process has also shown a continuing growth pattern (see Table 7 in the Appendix). In contrast, the other two processes have shown very little increase over the past few years. A more detailed description of these processes can be found in other references.[7,58,88,106]

According to 1962 data,[88] 60 plants use the by-product process, 22 plants use the synthesis process, and 15 plants use the salt-acid process. However, there are a total of only 88 plants producing hydrochloric acid, since some plants use more than one process. Production by State and process is given in Table 8 in the Appendix. The major producers of hydrochloric acid are listed in Table 9 in the Appendix.

3.2.1 By-Product Process

The major commercial source of hydrochloric acid is the chlorination of organic compounds by chlorine gas. Thus, in any manufacturing process in which chlorine gas is used to replace hydrogen with chlorine in a compound, hydrogen chloride is produced as a by-product. Examples of such processes are the preparation of carbon tetrachloride using methane (Equation 1) and of chlorobenzene using benzene (Equation 2). The chlorination process may be used to prepare a desired end product, such as carbon tetrachloride or chlorobenzene, or may be used to prepare an intermediate for a non-chloro-containing end product, as in the preparation of phenol from benzene using chlorobenzene (Equations 2 and 3).

$$\underset{\text{(Methane)}}{CH_4} + 4Cl_2 \longrightarrow \underset{\text{(Carbon tetrachloride)}}{CCl_4} + 4HCl \qquad \text{(Equation 1)}$$

$$\underset{\text{(Benzene)}}{C_6H_6} + Cl_2 \longrightarrow \underset{\text{(Chlorobenzene)}}{C_6H_5Cl} + HCl \qquad \text{(Equation 2)}$$

$$\underset{\text{(Chlorobenzene)}}{C_6H_5Cl} + NaOH \longrightarrow \underset{\text{(Phenol)}}{C_6H_5OH} + NaCl \qquad \text{(Equation 3)}$$

Therefore, it is not possible to determine from the end products

of a company whether by-product hydrochloric acid is being produced if one is not familiar with each of the processes used to obtain the final product. Numerous chlorinated and nonchlorinated organic compounds are made in which hydrogen chloride is evolved as a by-product. In fact, approximately 70 percent of the chlorine produced today is used in the manufacture or preparation of organic compounds.[6] The ever-increasing use of chlorinated organic compounds is reflected in the production of hydrochloric acid using by-product recovery (see Table 7 in the Appendix).

The effluent gas from the chlorination of an organic compound contains not only hydrogen chloride but also various amounts of air, chlorine gas, and organic products, depending on such factors as initial organic reactant and conditions used. Therefore, the recovery system for the hydrogen chloride or hydrochloric acid varies with the nature of the other impurities present in the effluent gas. For example, if the organic contaminants are low-boiling, the hydrogen chloride is removed first by means of a water absorption system (see Section 4). On the other hand, if the organic impurities are high-boiling, they are removed by condensation before the hydrogen chloride is absorbed. To obtain anhydrous hydrogen chloride, the effluent gas is fed into a condenser or distillation apparatus for separation of the different products. Several recovery systems are reported in the literature.[16,47,63,77,98] Normally, the hydrochloric acid produced by this method contains organic impurities and may require further purification.

Although hydrochloric acid produced as a by-product is collected for use and sale by some companies, in other cases the acid emissions may only be treated to avoid air pollution; and in still others, nothing may be done about the emissions.

3.2.2 Salt-Acid Process

In this process, common salt (sodium chloride, NaCl) is reacted with sulfuric acid (60^{o} or 66^{o} Baume). The reaction takes place in two steps: first, hydrogen chloride and sodium acid sulfate are formed, and second, sodium acid sulfate is further reacted with sodium chloride to yield more hydrogen chloride and sodium sulfate (normal sulfate). (See Equations 4 and 5.) In cases in which sodium acid sulfate is available—e.g., as a by-product in the manufacture of nitric acid—the acid sulfate is used directly as shown in Equation 5.

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl \qquad \text{(Equation 4)}$$

$$NaHSO_4 + NaCl \longrightarrow Na_2SO_4 + HCl \qquad \text{(Equation 5)}$$

Generally, the salt and a slight excess of acid are heated to 1,400 to $1,600^{o}F$ in a Mannheim oven. The reactants are continuously fed into the center of the furnace, and the salt cake that forms is removed at the periphery, where it is discharged continuously through a chute for transfer to storage. The effluent gas contains 30 to 70 percent (by volume) hydrogen chloride, as well as salt dust, air, and small traces of chlorine. This gas is passed through dust removal equipment, such as settling chambers or cyclones, and then cooled to approximately $100^{o}F$ by means of tube coolers or packed towers.[50,58]

A further purification system, usually coke filtering, is used to remove sulfuric acid mist and the remaining fine dust particles. After this final step, the hydrogen chloride is collected by absorption methods described in Section 4.

One of the major producers of hydrochloric acid in the United States uses the Hargreaves process.[58,92] In this process the salt, sodium chloride, is reacted directly with sulfur dioxide in the presence of steam and air (Equation 6). The sulfur dioxide, obtained by burning sulfur, is passed into a series of vertical chambers which have perforated trays for the salt. The system is designed so that the sulfur dioxide stream is first passed through a chamber containing nearly spent salt and lastly through a chamber containing the raw salt. The system temperatures vary from 1,000°C initially to 800°C in the final chambers of raw salt. The end gas then is passed through the absorption system to obtain the hydrochloric acid.

$$4NaCl + 2SO_2 + O_2 + 2H_2O \longrightarrow 2Na_2SO_4 + 4HCl \quad \text{(Equation 6)}$$

Hydrogen chloride emissions from the salt-acid process are higher than those from either of the other two processes.[7] In the Mannheim furnace operations, losses of hydrogen chloride can occur through leaks at the furnace, removal of hot salt cake, or from the tail gas emissions.[91,92] In the more modern furnaces, emissions are controlled by use of an exhaust fan installed after the absorber system to maintain the pressure slightly below atmospheric level at the furnace; the hot

salt cake is also precooled in a water-cooled screen conveyor before dumping. However, if large leaks occur in the system, the system becomes blocked, or the exhaust fan fails, the furnace can lose its draft, and emissions into the atmosphere can occur around the furnace, particularly at the doors and at the salt cake discharge.[50] Short periods of emissions can occur if the furnace door is opened to break up large lumps of salt that interfere with proper operation of the furnace.

Emissions resulting from upsets in the hydrogen chloride absorption system, which is common to all three processes, are discussed in Section 4.

3.2.3 Chlorine-Hydrogen Synthesis

The advantage of the chlorine-hydrogen synthesis process is that a hydrochloric acid is produced that is very pure, depending on the purity of the reactants. In this process, chlorine is burned in a slight excess of hydrogen in a reactor or combustion chamber.[50,106] The resulting product is 98 to 99.7 percent pure.[106] Since a mixture of hydrogen and chlorine is explosive, several safety provisions are incorporated into the system, which is completely enclosed. Thus, there is very little emission of hydrogen chloride in this process.[7] The product gas is passed through a gas-cooling system and then an absorption system similar to that used for the salt-acid process to give hydrochloric acid. If hydrogen chloride is desired, only gas-cooling equipment is necessary.

3.3 Product Sources

Hydrochloric acid and hydrogen chloride have a wide variety of uses;[58,76] major uses are in the manufacture of organic and inorganic chemicals, production of metals, the cleaning of metal and other materials, food processing, and acidification of oil wells. The consumption of hydrochloric acid for these uses in 1963 is given in Table 10 in the Appendix. The consumption by certain industries for 1958 and 1963 is given in Table 11 in the Appendix. As shown by the latter table, the demand for hydrochloric acid is increasing (see also Table 7, Appendix). The use of hydrochloric acid in steel pickling, vinyl plastics, oil well acidizing, and industrial cleaning and chemical products is also increasing.

However, even with the growing demand, there has been an oversupply of hydrochloric acid in recent years.[58,88] This fact, plus the increase in stream pollution by the acid, has made disposal of hydrochloric acid an expanding problem. One possible solution for the oversupply problem is the use of hydrochloric acid to manufacture chlorine.[58] According to reports by trade sources, the oversupply has shown a gradual decline.[20]

3.3.1 Manufacture of Chemicals

Nearly half of the hydrochloric acid produced is used in the manufacture of organic chemicals, such as chlorinated organic compounds, including the manufacture of alkyl chlorides from olefins and chlorides from alcohols. It is also used in the presence of oxygen (oxyhydrochlorination) to prepare

polychlorinated alkyl compounds and chlorinated aromatic compounds. Other uses occur in the production of dyes and dye intermediates and in the preparation of pharmaceutical chemicals, such as various amine hydrochloride salts, aconitic acid, adipic acid, and citric acid. In the production of chlorinated polymers, hydrochloric acid is used in the preparation of intermediate monomers, such as chloroprene and vinyl chloride. In addition, it is used as a solvent and a catalyst in organic reactions involving isomerization, polymerization, and alkylation.

Only about 5 percent of the hydrochloric acid produced is used for preparing inorganic chemicals, such as metal chlorides, alumina, phosphoric acid, titanium dioxide, silica gel, and paint pigments.[58,76,88,96] Recently, hydrochloric acid has been used to manufacture chlorine by electrolysis or oxidation methods.

3.3.2 Metal Production

Metal production consumes approximately 17 percent of the hydrochloric acid produced. It is used in many metallurgical extraction processes for treating various high-grade ores, including those which yield germanium, manganese, radium, tantalum, tin, and vanadium. Hydrochloric acid is also being considered as a substitute for sulfuric acid in treating low-grade ores. The Dron process for obtaining magnesium from seawater uses hydrochloric acid. This acid is also used as an etching medium for chemical milling of metals such as aluminum, magnesium, steel, and titanium.

3.3.3 Other Uses

Another major use, accounting for approximately 18 percent of the production of hydrochloric acid, is in the Dowell process for activating petroleum wells. Inhibited hydrochloric acid is used to improve oil well porosity and well flow or production by acidizing the formation.

Approximately 7 percent of the hydrochloric acid produced is used primarily for pickling and cleaning metal products and removing oxides and scale from boilers and heat-exchange equipment.

A small amount of hydrochloric acid is used in food processing, including hydrolysis of proteins and starch in the preparation of dextrose and starch syrups, manufacture of monosodium glutamate, and reactivation of bone char and charcoal in sugar refining.

It is also used in chlorinating and reclaiming rubber, coagulating latex, fluxing babbitt metals, detanning hides following depilation, and etching airport runways in preparation for resurfacing with bonded concrete. It is also an ingredient in tanning and dye liquors.

3.4 Other Sources

Atmospheric emissions of hydrochloric acid result from a large number of sources other than the manufacture and use of this acid. These other sources include heating or burning of chloride-containing materials in the presence of organic compounds or other hydrogen-containing substances. Chlorides

are also widespread in nature and in many natural products. Moreover, many manufactured products contain chloride, such as polyvinyl chloride plastics. When these materials are burned, incinerated, or perhaps just heated, hydrochloric acid can be evolved as a predicted or unpredicted product. The examples discussed in this section give an indication of some of the possible emission sources.

3.4.1 Coal

Burning coal may be one of the major contributors to hydrochloric acid air pollution. Chlorine is present in coals, mostly in the form of inorganic chloride salts[27] that are soluble in water.[22] When coal burns, most of the chloride salts are converted to hydrogen chloride,[57,58] which is then emitted into the atmosphere.

Analysis of United States coals shows that the chlorine content ranges from 0.01 to 0.56 percent.[1,51,78,89] Table 12 in the Appendix indicates the chlorine content of some selected coals in the United States. The Central and Appalachian areas, which have high-chlorine-content coals, are also the areas which consume most of the coal for heat and energy.[51]

Piper and Van Vliet[80] found that in burning coal containing 0.066 percent chlorine, 49 ppm of hydrogen chloride were emitted at the stack, meaning that 60 percent of the chlorine originally in the coal was converted to hydrogen chloride. Iapalucci, Demski, and Bienstock[51] performed experiments with pulverized coal containing 0.1 to 0.4 percent

chlorine at carbon combustion efficiencies of 94 to 98 percent. Under these conditions, they found that 93 to 98 percent of the chlorine was emitted as hydrogen chloride and the remainder left in the ash. To verify these results under actual conditions, the stack of a local power plant was sampled after burning a bituminous coal containing 0.087 percent chlorine. Analysis showed that only 1.5 percent of the chlorine was retained in the ash, and the balance was emitted in the stack gas as hydrogen chloride.

Furthermore, the amount of hydrochloric acid pollution by burning coal may be increased when calcium chloride is added to the coal as an antifreeze or dust-proofing agent.[53]

A potentially large amount of hydrochloric acid pollution may result from coal burning. For example, it is estimated that 671 million short tons of bituminous coal will be consumed in 1975.[11] Assuming that the average chlorine content of the coal is 0.2 percent and that 95 percent of this is converted to hydrochloric acid, then approximately 1.3 million short tons of hydrochloric acid will be produced from coal burning in 1975. For comparison, manufacture of hydrogen chloride and hydrochloric acid was 1.6 million short tons in 1967.[23] Iapalucci, Demski, and Bienstock[51] estimated on a similar basis (i.e., 0.2 percent chlorine coal) that an 800-MW power plant will emit from the stack 11,300 standard cubic feet of hydrogen chloride each hour, or 4,560 tons each year.

3.4.2 Fuel Oil

Fuel oils contain small amounts of chlorides and can therefore emit hydrogen chloride when burned. A recent study on fuel oils[94] cited two 1938 reports on chloride emissions. In one report[109] the chloride content of the ash was given as 0.1 and 4.6 percent by weight for oils found in Kansas and Texas, respectively. The other report[117] indicated that the maximum hydrogen chloride content in emissions was approximately 46 ppm in the stack gas, or approximately 1 pound per 1,000 pounds of oil. It has been reported that 500 pounds of hydrogen chloride per day per 100,000 persons is produced by using oil for domestic heating.[30] In comparison, the value is four times higher for domestic heating using coal.

3.4.3 Automobile Exhaust

Gasolines which contain tetraethyl lead (TEL), tetramethyl lead (TML), or other lead additives also usually contain ethylene chloride or ethylene bromide. These organic halide compounds are used as lead scavengers; that is, these halides will react with the lead to form volatile lead halides which can be emitted with the exhaust gases and, therefore, prevent lead deposits in the automobile engine. An example of an additive mixture for gasoline is given in Table 1.

TABLE 1

"ETHYL" ANTIKNOCK COMPOUND-TEL MOTOR 33 MIX[101]

Compound	Weight (percent)
Tetraethyl lead	57.5
Methyl cyclopentadieny-manganese tricarbonyl	7.0
Ethylene dibromide	16.7
Ethylene dichloride	17.6
Other (dye, inerts)	1.2

During gasoline combustion, hydrogen chloride or hydrochloric acid can form and be emitted into the air. Rose[83] feels that hydrochloric acid is present in automobile exhaust but did not know of any quantitative data available. He mentioned that the exhaust condensates were very acidic, about pH 2.

3.4.4 Burning of Chloride-Containing Plastics

Several of the plastics used today contain organically bound chlorine; examples of some of the more common ones are polyvinyl chloride (approximately 57 percent chlorine), polyvinylidene chloride (approximately 73 percent chlorine), and neoprene (approximately 40 percent chlorine). In addition, organic chlorides are added to other types of plastics and materials as fire-retardants. Chloride-containing plastics are used in making plastic films, containers, seat covers,

wire insulation, and many other materials. When these chloride plastics are heated or burned, hydrogen chloride is evolved.[12,18,54,71,81] Studies have been conducted with polyvinyl chloride films[12,81] to determine the type and quantity of gases evolved. In one investigation,[12] a sample was heated at a rate of 3°C per minute; upon reaching 280°C a rapid weight loss started and continued until about 300°C. During this period a 60 percent weight loss was found, and analysis showed that almost all the chloride had been evolved as hydrogen chloride. In another study,[81] it was found that hydrogen chloride evolved at 100°C; moreover, the rate of evolution depended on the length of the heating period. The rate of hydrogen chloride evolution for 1 hour at 100°C was 8,000 $\mu g/m^3$; after 2 hours, 12,000 $\mu g/m^3$; and after 3 hours, 20,000 $\mu g/m^3$.

Thus, open burning or incineration of chlorinated plastics is a probable source of hydrochloric acid pollution. Without effective control measures, this problem will intensify with the increased use of plastics projected for the future.

3.4.5 Burning of Paper Products

Analysis of paper products indicates that the chloride content is low,[10,13] approximately 0.03 to 0.16 percent by weight. Nevertheless, two examples cited in the literature demonstrate that the amounts of hydrochloric acid emissions from the incineration of paper can cause injury to plants.[13]

In both examples (see Section 2.3.2), the plant injury was caused by hydrochloric acid emissions from a hospital incinerator burning trash consisting of 80 to 90 percent paper products. Additional studies indicated that 53 to 95 percent of the chloride in paper products is lost on heating at 900°C.

3.4.6 DDT Production

DDT (dichlorodiphenyltrichloroethane) is a common pesticide manufactured from chloral, chlorobenzene, and sulfuric acid[2] (see Equation 7).

$$\underset{\text{(Chloral)}}{CCl_3CHO} + 2C_6H_5Cl \xrightarrow{H_2SO_4} CCl_3CH(C_6H_4Cl)_2 + H_2O \qquad \text{(Equation 7)}$$

As seen from the reaction equation, hydrochloric acid is neither a reactant nor a product of the desired reaction. However, the primary contaminate in the emissions is hydrochloric acid from decomposition of chloral. The total amount of effluent gases has been estimated as about 1 percent of the weight of DDT produced.

This is an example of a manufacturing process in which hydrochloric acid is considered neither a reactant nor a product but, nevertheless, is part of the effluent gas stream. In this case, the hydrochloric acid emissions are due to the decomposition of the chloride compounds used in the reaction.

3.4.7 Lemon Pulp Extraction

One company has reported on the extraction of lemon pulp with isopropyl alcohol at 120°F.[8] Besides the predictable emissions of the alcohol, the effluent vapor also contained

hydrochloric acid droplets. In this case, the company was aware of the content of the emissions and used an appropriate treatment system to control the emissions.

Although probably only a very minor source, this represents an example of the heating of organic matter at a low temperature (120°F) with the evolution of small quantities of hydrochloric acid.

3.5 Environmental Air Concentrations

No information has been found on environmental air concentrations of hydrochloric acid. However, Gorham[40] observed that in Great Britain, precipitation samples from urban areas exhibited a distinct correlation between chloride content and acidity in samples of pH less than 5.7.

4. ABATEMENT

The high solubility of hydrogen chloride in water and the low vapor pressures of even 20 percent hydrochloric acid solutions make collection of hydrogen chloride in water an effective and inexpensive method of control.

Thus in the manufacture of hydrochloric acid (or hydrogen chloride), the emission control system, which is also part of the system for obtaining hydrochloric acid from the hydrogen chloride, consists mainly of water absorption facilities. Different types of absorbers are used, but the systems generally consist of a packed tower or a cooling absorption tower followed by a packed tail tower.[50,58,106] The packed tower systems[50,58] normally include a connected set of S-bend tubes, followed by one or more towers in series. Cold water is added at the last or tail tower and flows over into the previous tower. The concentration of hydrochloric acid in this water is thus increased from tower to tower until it reaches the S-bend tubes, where the acid solution attains its final strength. However, the packed tower systems are rapidly being replaced by cooled absorption systems because the latter are more efficient, economical, and compact. The cooled absorption tower designs may consist of either a countercurrent or co-current flow of gas and water. One type uses water-jacketed packed tantalum towers with countercurrent flow.[58] The most common system is the co-current falling film absorbers.[49,58,59] In this system, gas and weak acid solution

from the packed tail tower flow downward over vertical, water-cooled, wetted-wall columns. Where anhydrous chloride is the desired product, absorption systems are not used.[50]

It has been reported that the use of water scrubbing systems can reduce the emissions to less than 0.1 pound of hydrogen chloride per ton of acid produced, although emissions can be 30 times that amount with less effective equipment.[7] According to Faith et al.,[31] hydrogen chloride emissions can be reduced to a range of 0.1 to 0.3 percent by volume by the use of two or more tail towers in series. The emissions of hydrochloric acid may be high if an upset occurs in the absorption system due to either improper temperature control or insufficient feed water.[106]

Other systems that appear to be effective for the control of hydrochloric acid or hydrogen chloride emissions are the rotary brush scrubber[59] and the ejector venturi scrubber.[41] With the former system, collection efficiencies of 99.995 percent have been reported with an initial hydrogen chloride content of 610 g/m^3. In the latter system, scrubbing efficiency as high as 99 percent has been given for a single-stage unit for fumes containing up to 20 percent hydrogen chloride. The high solubility of hydrogen chloride in water accounts for the high degree of efficiency of these systems.

Dry solid adsorbents have also been studied for removal of hydrogen chloride vapors.[9,71] Adsorbents investigated include chromium oxinate[9] and basic salts[36] such as Beralyme,

soda lime, lithium carbonate, and silica-alumina mixtures. Chromium oxinate or tris-(8-hydroxyquinolinato)chromium(III) exhibited physical adsorption with anhydrous hydrogen chloride, but the adsorbing bed showed a tailing effect a long time before the exit gas concentration reached the entering concentration.

Studies by Iapalucci, Demski, and Bienstock[51] indicate that hydrochloric acid emissions from coal burning can be reduced by adding basic salts, such as sodium carbonate, potassium carbonate, calcium carbonate, and dolomite. Chlorine retention in the ash when a small amount of basic salt was added was 8.8 to 37.8 percent, compared to 7.9 percent without an additive.

5. ECONOMICS

No information has been found on the damage costs or economic losses due to the effects of hydrochloric acid air pollution on humans, animals, plants, or materials. In addition, no information has been found on the economic costs of abatement (installation and operation costs of control equipment and cost benefits of usable emissions).

Data on the production and consumption of hydrochloric acid are presented in Section 3.

6. METHODS OF ANALYSIS

All of the common methods of analysis for hydrochloric acid in air depend upon (1) measurement of acidity, (2) measurement of chloride ions, or (3) combination of the two measurements. Therefore, other strong acids (e.g., sulfuric acid, nitric acid) or other chloride salts (e.g., sodium chloride) can cause serious interference.

6.1 Sampling Methods

In most methods, hydrochloric acid is collected in impingers containing water.[4,25,105] The high solubility of hydrochloric acid in water yields excellent absorption efficiency.[66]

The results of one investigation indicate that certain phosphate salts, particularly silver phosphate, have a high collection efficiency for hydrochloric acid but do not absorb sulfur dioxide.[17] However, hydrobromic acid is also absorbed.

Preliminary studies indicate that liquid crystals may make effective and selective collection materials for hydrochloric acid and other gaseous pollutants.[33] Acid mists have also been collected on paper,[19] gelatinous film,[38,68,114] thin metal films,[67] and metal-coated glass slides.[43,48]

6.2 Qualitative Methods

The presence of hydrochloric acid or any other strong acid in air can be determined by passing the air over moist pH indicators such as methyl orange, congo red, or blue litmus papers. Hydrochloric acid or other chlorides can also

be detected by bubbling the air through water and adding silver nitrate. Depending on the concentration of chloride, the solution may show a slight turbidity, or yield a white to grayish precipitate which will not change on addition of nitric acid but will dissolve or disappear upon addition of ammonia.

6.3 Quantitative Methods

In the absence of other strong acids, hydrochloric acid samples which have been collected in water may be determined quantitatively by the usual direct titration methods with standard bases.[25]

A spectrophotometric method for determination of strong acids has been reported.[39,70] After the air sample is passed through water, methyl red is added to the acidic solution and the optical density at 530 mμ is determined. Normal concentrations of carbon dioxide and 1,000 μg of sulfur dioxide per m^3 of air do not interfere.

The size and quantity of acid mists have been determined by the use of both gelatinous films[38,68,114] and metal-coated glass slides.[43,48] The latter method is not affected by relative humidity. Through use of an electron microscope, it is possible to detect acid droplets with diameters of less than 0.1 μ.[48]

In the absence of soluble chloride salts, hydrochloric acid samples dissolve in water and may be determined by the standard methods for chloride determination,[99] including the

Mohr method,[99,100] absorption indicator method,[32,60] and the modified Volhard method.[15] These methods have a sensitivity of approximately 18,000 μg of chloride per liter. For very small amounts of chloride in air, the determination can be made turbidimetrically or nephelometrically.[24,79,99] The hydrochloric acid solution is treated with silver nitrate and the turbidity determined spectrophotometrically; sensitivity is in the microgram range. Recently, a method has been developed for determining chloride colorimetrically.[115,116] This method is based on the yellow color produced by the iron(III) chloro complex in perchloric acid with a sensitivity of approximately 1,000 $\mu g/m^3$ of chloride. This method suffers from interference from mercury and sulfate ions and is affected by the relative humidity of the air. There is a neutron activation technique for determining chloride in particulates with a sensitivity of approximately 0.06 $\mu g/m^3$.[56]

An automated analysis method for chloride is used by the National Air Sampling Network.[110] This method is based on the reaction of chloride with mercury thiocyanate to yield thiocyanate ions. Thiocyanate ions react with ferric ions to form the stable red complex, hexacyanatoferrate ion, which can be determined spectrophotometrically at 460 mμ. The relative standard deviation for chloride is 1.0 $\pm$ 0.1 μg/ml.

Since air samples usually contain other acids as well as chlorides, these methods are not generally applicable. There are no methods available that are free from interference

by all other possible pollutants. However, an air sample containing a mixture of sulfur oxides, hydrochloric acid, and other chlorides can be analyzed by combining the methods reported in two papers.[4,105] The air sample is passed through an aqueous solution of hydrogen peroxide. The aqueous solution is then divided into three parts for three separate analyses: sulfate, chloride, and hydrogen ion. From these results the amount of each component can be determined.

7. SUMMARY AND CONCLUSIONS

Hydrogen chloride reacts rapidly with the moisture in the air and is generally found in the ambient atmosphere as hydrochloric acid. The acid at low concentrations, 15,000 to 75,000 $\mu g/m^3$ (10 to 50 ppm), irritates primarily the mucous membranes of the eyes and upper respiratory tract in both humans and animals. Prolonged exposures to low concentrations of hydrochloric acid can also erode the teeth. Work is intolerable after more than 60 minutes in atmospheres containing approximately 75,000 to 150,000 $\mu g/m^3$ (50 to 100 ppm) of hydrochloric acid. Higher concentrations (approximately 1,500,000 $\mu g/m^3$ or 1,000 ppm) can attack the mucous membranes, causing inflammation of the upper respiratory system and resulting in pulmonary edema or spasm of the larynx, which can be fatal. A wide variety of plant life is susceptible to the toxic effects of hydrogen chloride or hydrochloric acid. Several examples of plant damage due to hydrochloric acid emissions have been reported in the literature. The primary effect on plants is a discoloration or bleaching of the leaves. The threshold for visible damage was originally reported as 75,000 to 150,000 $\mu g/m^3$ (50 to 100 ppm) of hydrogen chloride. However, recent studies indicate that the threshold for many plants is less than 10 ppm for 4-hour exposures. The strong acidic properties of hydrochloric acid make it extremely corrosive to most metals.

Some countries have established ambient air quality standards for hydrochloric acid, including West Germany (approximately 750 $\mu g/m^3$ or 0.5 ppm as a mean 30-minute average) and Russia (approximately 15 $\mu g/m^3$ or 0.009 ppm as a 24-hour average).

The production rate since 1961 has shown a general increase of approximately 9 percent. Hydrogen chloride is produced by three main processes in the United States: acid-salt, direct synthesis, and the by-product process from chlorination of organic compounds. The latter process, the major production source, has shown a steady increase. Many organic chlorinating processes and other organic processes involving chlorinated compounds may produce hydrogen chloride as a by-product, but it may not be economically feasible to recover the product for other uses. Hydrochloric acid is produced by absorbing the hydrogen chloride gas into water.

Hydrochloric acid (or hydrogen chloride) is primarily used to manufacture inorganic and organic chemicals, the latter accounting for almost 50 percent of the production in 1963. Other major uses include metal production, oil-well acidizing, metal and industrial cleaning, and food processing.

Another potential source of emissions of hydrochloric acid is the heating or burning of chlorinated materials. The burning of coal appears to be a possible major source of hydrochloric acid pollution, since the chloride in coal is

converted to over 90 percent hydrogen chloride during the burning process. Similarly, the burning of chlorinated plastics and paper can be an emission source, and possibly the burning of fuel oil and gasoline as well.

No information has been found on the concentrations of hydrochloric acid in the atmosphere. Hydrogen chloride emissions from commercial processes can be effectively controlled by the equipment that is available today. Systems now in use include packed water scrubbing towers and cooled absorption towers. Emissions from coal burning may be decreased by the addition of basic salts to the coal before burning.

No information has been found on costs for the control of hydrochloric acid pollution or for costs incurred by damage to humans, animals, plants, and materials as a result of hydrochloric acid emissions.

No continuous monitoring methods are available for measuring the hydrochloric acid content of environmental air. The common methods used measure either the acidity or chloride content of the air sample, and therefore suffer from interference from other acids and chlorides present in the environmental air.

Based on the material presented in this report, further studies are suggested in the following areas:

(1) Determination of the amount of hydrochloric acid present in the atmosphere of heavily populated areas,

particularly near the source of production and near coal-burning establishments and incinerators.

(2) Evaluation of the effects of low concentrations of hydrochloric acid on humans, animals, plants, and materials.

(3) Determination of the contribution of automobile exhausts, incinerators, and other combustion sources to hydrochloric acid air pollution.

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APPENDIX

APPENDIX

TABLE 2

PROPERTIES OF HYDROGEN CHLORIDE AND HYDROCHLORIC ACID[49,76]

Properties	Hydrogen Chloride (HCl)[a]	Hydrochloric Acid (HCl, aqua)[b]
Color, odor, normal state	Colorless gas, pungent, irritating odor, fumes in air	Colorless liquid; sometimes yellowish due to impurities (iron, arsenic, chlorine, and organic matter); pungent and irritating odor
Boiling point	-85°C (-121°F)	Aqueous solution containing 20.24% HCl: 110°C (230°F)
Melting point	-111°C (-168°F)	27.92% HCl: -42°C (-43.6°F) 37.14% HCl: -74°C (-101.2°F)
Hygroscopicity	Very hygroscopic	Hygroscopic
Density	1.6397 g/l (0°C, 760 mm)	20.04% HCl: 1.1006 g/l 37.14% HCl: 1.1885 g/l
Heat of fusion	476-504.5 g-cal/mole	
Heat of vaporization	3860±4 g-cal/mole	

(continued)

TABLE 2 (Continued)

PROPERTIES OF HYDROGEN CHLORIDE AND HYDROCHLORIC ACID[49,76]

Properties	Hydrogen Chloride (HCl)[a]	Hydrochloric Acid (HCl, aqua)[b]
Reactivity	Non-corrosive when dry. Reacts rapidly with many organic materials	Highly corrosive to moist metals with evolution of hydrogen gas. Reacts with basic salts (metallic oxides and carbonates)
Solubility in H_2O) ($g/100g\ H_2O$)	82.3 (0°C) 67.3 (30°C) 63.3 (40°C) 59.6 (50°C) 56.1 (60°C)	

[a]Also called hydrochloric acid, anhydrous.

[b]Also called muriatic acid.

APPENDIX

TABLE 3

SUMMARY OF REPORTED EFFECTS OF INHALATION OF HYDROGEN CHLORIDE BY HUMANS

Concentration (ppm)*	Exposure Time	Effects or Comments	Reference
50-100		Work is impossible	45,72
10-50		Work is difficult but possible	45,72
10		Work is undisturbed	45,72
1,300-2,000	Few min	Lethal	52,103
1,000-1,300	30-60 min	Dangerous	52
50-100	60 min	Intolerable	35,44,52,87
35		Irritation of throat after short exposure	87
1,000-2,000		Brief exposures are dangerous	87
10		Irritation	113
5		No organic damage	113

(continued)

APPENDIX

TABLE 3 (Continued)

SUMMARY OF REPORTED EFFECTS OF INHALATION OF HYDROGEN CHLORIDE BY HUMANS

Concentration (ppm)*	Exposure Time	Effects or Comments	Reference
10		Odor threshold value	105
0.067-0.134		Odor threshold value	28,29
0.402		Concentration for threshold reflex effect on optical chronaxie	28,29
0.134		Concentration for threshold reflex effect on eye sensitivity to light	28,29
0.335		Concentration for threshold effect on digito-vascular toxicity	28,29
0.067-0.134		Threshold concentrations of change in the rhythm and depth of respiratory movement	28,29
1-5		Odor threshold value	45

*1 ppm = 1,470 $\mu g/m^3$ at 25°C.

APPENDIX

TABLE 4

SUMMARY OF REPORTED EFFECTS OF INHALATION OF HYDROGEN CHLORIDE ON ANIMALS

Species	Concentration (ppm)*	Exposure Time	Effects or Comments	Reference
Rabbits	4,300	30 min	Fatal in some cases, due to laryngeal spasm, laryngeal edema, or rapidly developing pulmonary edema	45,69
Guinea pigs	4,300	30 min	Fatal in some cases, due to laryngeal spasm, laryngeal edema, or rapidly developing pulmonary edema	45,69
Cats	3,400	90 min	Death after 2 to 6 days	45,64
Rabbits	3,400	90 min	Death after 2 to 6 days	45,64
Guinea pigs	3,400	90 min	Death after 2 to 6 days	45,64
Cats	1,350	90 min	Severe irritation, dyspnea, and clouding of the cornea	45,64
Rabbits	1,350	90 min	Severe irritation, dyspnea, and clouding of the cornea	45,64

(continued)

APPENDIX

TABLE 4 (Continued)

SUMMARY OF REPORTED EFFECTS OF INHALATION OF HYDROGEN CHLORIDE ON ANIMALS

Species	Concentration (ppm)*	Exposure Time	Effects or Comments	Reference
Guinea pigs	1,350	90 min	Severe irritation, dyspnea, and clouding of the cornea	45,64
Rabbits	670	2 hr	Fatal in some cases	45,69
Guinea pigs	670	2 hr	Fatal in some cases	45,69
Rabbits	300	6 hr	Corrosion of the cornea and upper respiratory irritation	45,64
Guinea pigs	300	6 hr	Corrosion of the cornea and upper respiratory irritation	45,64
Rabbits	100-140	6 hr	Only slight corrosion of the cornea and upper respiratory irritation	45,64
Guinea pigs	100-140	6 hr	Only slight corrosion of the cornea and upper respiratory irritation	45,64

(continued)

APPENDIX

TABLE 4 (Continued)

SUMMARY OF REPORTED EFFECTS OF INHALATION OF HYDROGEN CHLORIDE ON ANIMALS

Species	Concentration (ppm)*	Exposure Time	Effects or Comments	Reference
Rabbits	100	6 hr/day for 50 days	Slight unrest and irritation of the eyes and nose	45,82
Guinea pigs	100	6 hr/day for 50 days	Slight unrest and irritation of the eyes and nose	45,82
Pigeons	100	6 hr/day for 50 days	Slight unrest and irritation of the eyes and nose	45,82
Monkey	33	6 hr/day 5 days/week for 4 weeks	No immediate toxic effects and no pathological changes	69
Rabbit	33	6 hr/day 5 days/week for 4 weeks	No immediate toxic effects and no pathological changes	69
Guinea pig	33	6/hr/day 5 days/week for 4 weeks	No immediate toxic effects and no pathological changes	69

(continued)

APPENDIX

TABLE 4 (Continued)

SUMMARY OF REPORTED EFFECTS OF INHALATION OF HYDROGEN CHLORIDE ON ANIMALS

Species	Concentration (ppm)*	Exposure Time	Effects or Comments	Reference
Rabbits	60	5 min	Cessation of ciliary activity without recovery	21
Rabbits	30	10 min	Cessation of ciliary activity without recovery	21

*1 ppm = 1,470 $\mu g/m^3$ at 25°C.

APPENDIX

TABLE 5

SUMMARY OF REPORTED TOXIC EFFECTS OF HYDROGEN CHLORIDE EXPOSURE ON PLANTS

Species	Concentration (ppm)*	Exposure Time	Effects or Comments	Reference
Plants	10-50		No leaf damage	113
Plants	100-1,000		Leaf damage	113
Sugar beets	10	Few hr	Threshold for marking	107
Viburnum seedlings	5-20	24 hr	Leaves rolled at the edges, withered, shrunk, faded, and necrotic	42
Beech	1,000	1 hr	Local lesions produced	42
Oak	1,000	1 hr	Local lesions produced	42
Maple	2,000		Marginal leaf scorch	42
Birch	2,000		Marginal leaf scorch	42
Pear	2,000		Marginal leaf scorch	42

(continued)

APPENDIX

TABLE 5 (Continued)

SUMMARY OF REPORTED TOXIC EFFECTS OF HYDROGEN CHLORIDE EXPOSURE ON PLANTS

Species	Concentration (ppm)*	Exposure Time	Effects or Comments	Reference
Viburnum seedlings	5-20	48 hr	Plants died	42
Larch	5-20	48 hr	Plants died	42
Fir	1,000	1 hr	Local lesions formed	42
Spruce	2,000	1 hr/day for 80 days	No apparent injury	42
Tomato plants	5	2 hr	Developed interveinal bronzing followed by necrosis within 72 hours after exposure	93
Liriodendron tulipifera	3	4 hr	Threshold for visible injury	74
Ainus glutinosa	6	4 hr	Threshold for visible injury	74
Prunus serotina	6	4 hr	Threshold for visible injury	74

(continued)

APPENDIX

TABLE 5 (Continued)

SUMMARY OF REPORTED TOXIC EFFECTS OF HYDROGEN CHLORIDE EXPOSURE ON PLANTS

Species	Concentration (ppm)*	Exposure Time	Effects or Comments	Reference
Acer saccharus	7	4 hr	Threshold for visible injury	74
Acer platanoides	7	4 hr	Threshold for visible injury	74
Quercus rubus	13	4 hr	No visible injury	74
Pinus strobus	8	4 hr	Threshold for visible injury	74
Psaudotsuga mantissii	10	4 hr	Threshold for visible injury	74
Abies balsamea	10	4 hr	Threshold for visible damage	74
Pinus abies	19	4 hr	Threshold for visible damage	74
Pinus nigra	18	4 hr	No visible damage	74

(continued)

APPENDIX

TABLE 5 (Continued)

SUMMARY OF REPORTED TOXIC EFFECTS OF HYDROGEN CHLORIDE EXPOSURE ON PLANTS

Species	Concentration (ppm)*	Exposure Time	Effects or Comments	Reference
Thuja occidentalis	43	4 hr	No visible damage	74
Spruce seedlings	<50	20 min	Plants died	61

*1 ppm = 1,470 $\mu g/m^3$ at 25°C.

APPENDIX

TABLE 6

EMISSIONS OF HYDROCHLORIC ACID IN SELECTED AREAS OF NIAGARA COUNTY, N.Y.[3]

Community	HCl Emitted (tons/year)
Cities:	
Lockport	187
Niagara Falls	3,436
North Tonawanda	149
Towns:	
Cambria	5
Hartland	5
Lewiston	191
Lockport	9
Newfane	16
Niagara	11
Pendleton	4
Porter	10
Royalton	7
Somerset	3
Wheatfield	24
Wilson	6
Villages:	
Barker	3
Lewiston	3
Middleport	8
Wilson	3
Youngstown	3
Total	4,083

APPENDIX

TABLE 7

HYDROCHLORIC ACID PRODUCTION IN THE UNITED STATES, 1958-1967[23]

Year	Hydrochloric Acid* Total HCl (short tons)	Process: Salt-Acid (short tons)	(percent)	Synthesis (short tons)	(percent)	By-Product and Others (short tons)	(percent)
1958	826,022	107,036	13.0	162,282	19.6	556,704	67.4
1959	955,914	100,008	10.4	165,751	17.3	690,155	72.3
1960	970,167	90,461	9.3	148,304	15.3	731,402	75.4
1961	910,967	87,073	9.5	118,059	13.0	705,835	77.5
1962	1,052,116	105,830	10.1	92,117	8.8	854,169	81.8
1963	1,053,502	128,652	12.2	92,276	8.8	832,574	79.0
1964	1,236,824	136,051	10.0	95,606	7.7	1,005,167	82.3
1965	1,370,092	138,121	10.1	99,043	7.2	1,132,928	82.7
1966	1,519,372	139,778	9.2	108,028	7.1	1,271,566	83.7
1967	1,597,682 (preliminary)	137,515	8.6	114,003	7.1	1,346,164	84.3

*Includes anhydrous hydrogen chloride.

APPENDIX

TABLE 8

PRODUCTION OF HYDROCHLORIC ACID BY PROCESS AND STATE[88]

State	Number of Plants Using Each Process			
	Salt-Acid	Direct Synthesis	By-Product	Total
Massachusetts	1		1	2
New Hampshire		1		1
New Jersey	3		7	10
New York		3	5	6*
Pennsylvania			1	1
Alabama			2	2
Delaware	1			1
Georgia		1	2	3
Kentucky	1	3	3	5*
Louisiana	2	2	3	5*
Maryland			1	1
Tennessee			1	1
Texas	1	3	8	11*
Virginia	1	1		2
West Virginia			6	6
Illinois	1		2	3
Indiana	1		2	3
Kansas		1		1
Michigan		2	6	7*
Missouri			1	1
Ohio	2	1	4	6*
California		2	3	5
Nevada			1	1
New Mexico	1			1
Washington		2	1	3
Total	15	22	60	88*

*Some plants use more than one process.

APPENDIX

TABLE 9

MAJOR PRODUCERS OF HYDROCHLORIC ACID (MURIATIC ACID) IN THE UNITED STATES[108]

Company	Location
Allen, L. B., Co., Inc.	Schiller Park, Ill.
Allied Chemical Corp., Industrial Chemicals Div.	Morristown, N.J.
American Cyanamid Co., Industrial Chemicals Div.	Wayne, N.J.
American Oil & Supply Co.	Newark, N.J.
Baker, J. T., Chemical Co.	North Phillipsburg, N.J.
Bay Chemical Co.	Chicago, Ill.
Berg Chemical Co., Inc.	New York, N.Y.
Big Ben Chemicals & Solvents, Inc.	Chicago, Ill.
Calcine Chemical Co.	Jersey City, N.J.
Celanese Corp. of America, Chemical Div.	New York, N.Y.
Central Chemical Div.	Calumet City, Ill.
Diamond Alkali Co.	Cleveland, Ohio
Dover Chemical Corp.	Dover, Ohio
Dow Chemical Co.	Midland, Mich.
Dowell Div.	Tulsa, Okla.
Essex Chemical Corp.	Clifton, N.J.
General Aniline & Film Corp.	New York, N.Y.
Globe Chemical Co., Inc.	Cincinnati, Ohio
Haviland Products Co.	Grand Rapids, Mich.
Hooker Chemical Corp. Industrial Chemicals Div.	Niagara Falls, N.Y.
Hubbard-Hall Chemical Co.	Waterbury, Conn.
International Minerals & Chemical Corp.	Skokie, Ill.
International Minerals & Chemical Corp.	Chicago, Ill.
Johnson Mfg. Co.	Princeton, Iowa
Jones Chemicals, Inc.	Caledonia, N.Y.
Knight, Maurice A., Co.	Akron, Ohio
Kraft Chemical Co.	Chicago, Ill.
McKesson & Robbins, Inc., Chemical Dept.	New York, N.Y.
Mercury Chemical Corp.	Metuchen, N.J.
Monarch Chemical Works, Inc.	Omaha, Nebr.
Monsanto Inorganic Chemicals Div.	St. Louis, Mo.
National Zinc Co., Inc.	New York, N.Y.
Neville Chemical Co.	Pittsburgh, Pa.
Nitine Inc.	Whippany, N.J.
Octagon Process Inc.	Edgewater, N.J.

(continued)

APPENDIX

TABLE 9 (Continued)

MAJOR PRODUCERS OF HYDROCHLORIC ACID (MURIATIC ACID) IN THE UNITED STATES[108]

Company	Location
Olin Mathieson Chemical Corp.	New York, N.Y.
Pennsalt Chemical Corp.	Tulsa, Okla.
Phillipp Brothers Chemicals Inc.	New York, N.Y.
Potash Co. of America	Carlsbad, N. Mex.
PPG Industries Chemical Div.	Pittsburgh, Pa.
Riverside Chemical Co., Inc.	North Tonawanda, N.Y.
Robinson Bros. Chemicals Inc.	Brooklyn, N.Y.
Rohm & Haas Co.	Philadelphia, Pa.
Seaway Chemical Corp.	Buffalo, N.Y.
Siegel Chemical Co., Inc.	Brooklyn, N.Y.
Solvent Chemical Co.	Malden, Mass.
Smith-Douglass Co., Inc.	Norfolk, Va.
Stauffer Chemical Co. Industrial Chemical Div.	New York, N.Y.
Tenneco Chemicals Inc.	New York, N.Y.
Triple-X Chemical Laboratories, Inc.	Chicago, Ill.
United States Rubber Co., Chemical Div.	Naugatuck, Conn.
Velsicol Chemical Corp., Tennsyn Div.	Chattanooga, Tenn.
Vulcan Materials Co., Chemicals Div.	Wichita, Kans.
Wittichen Chemical Co.	Birmingham, Ala.

APPENDIX

TABLE 10

CONSUMPTION OF HYDROCHLORIC ACID BY USES, 1963[58]

Uses	Approximate %	100% HCl (Short Tons)*
Organic chemicals	49	516,500
Inorganic chemicals	5	52,600
Metal production	17	179,000
Metal and industrial cleaning	7	73,700
Food processing	4	42,200
Oil well acidizing	18	189,500
Total	100	1,053,500

*Approximately calculated on basis of 1963 total production of 1,053,502 short tons (see Table 7, Appendix).

APPENDIX

TABLE 11

CONSUMPTION OF HYDROCHLORIC ACID BY SELECTED INDUSTRIES, 1963 and 1958[14]

Industry	100% HCl (Short Tons) 1963	1958
Organic chemicals[a]	438,746	280,822
Intermediate coal tar products	79,505	18,802
Inorganic chemicals[a,b]	51,200	24,400
Alkalies and chlorine	44,557	12,280
Plastics material and resins	13,993	36,754
Total	628,001	373,058

[a]Not elsewhere classified.

[b]Estimated from total money spent in 1958 and 1963 by inorganic chemical industries and prices paid during those periods by other industries.

TABLE 12

CHLORINE CONTENT OF SELECTED UNITED STATES COALS[95]

Source of Coal		Chlorine Content
State	Bed	(percent)
Ohio	Sharon	0.01
Illinois	No. 6	0.01
Indiana	No. 4	0.06
West Virginia	Pittsburgh	0.07
Pennsylvania	Lower Freeport	0.14
Illinois	Central Illinois	0.35
Oklahoma	Henryetta	0.46